hoped that the further survey now being made may indicate more clearly the nature of the modifications required.

We wish to express our warmest thanks to Prof. Sir Ernest Rutherford for his continued interest in these experiments and for his kindness in supplying the considerable quantities of emanation employed in the work. We are also indebted to Mr. Crowe for constructing and filling the emanation tubes.

Boundary Lubrication.—The Paraffin Series.

By W. B. Hardy, Sec. R.S., and Ida Doubleday.

(Received January 6, 1922.)

(A Report to the Lubrication Committee of the Department of Scientific and Industrial Research.)

In what is often called complete lubrication, the kind of lubrication investigated by Towers and Osborne Reynolds, the solid surfaces are completely floated apart by the lubricant. There is, however, another kind of lubrication in which the solid faces are near enough together to influence directly the physical properties of the lubricant. This is the condition found with "dry" or "greasy" surfaces. What Osborne Reynolds calls "boundary conditions" then operate, and the friction depends not only on the lubricant, but also on the chemical nature of the solid boundaries. Boundary lubrication differs so greatly from complete lubrication as to suggest that there is a discontinuity between the two states. In the former the surfaces have the property of static friction, and the resistance is some inverse function of the viscosity of the lubricant. In complete lubrication static friction is absent and the resistance varies directly with the viscosity of the lubricant. Boundary lubrication is alone considered in this paper.

The enquiry is limited to the lubricating qualities of normal paraffins and their related acids and alcohols. The molecules of the substances employed, therefore, consist either of a simple chain of carbon atoms to which are attached atoms of hydrogen, or of such a chain loaded at one end with the hydroxyl group—OH, or the carboxyl group—COOH.

Attention was concentrated chiefly on three variables—the quantity of lubricant present, the composition of the solid faces, and the chemical constitution of the lubricant. The relations disclosed by the experiments are of surprising simplicity, whilst their interpretation is difficult. For this reason the paper is divided into two parts, the first devoted to the results of experiment and the second to theory.

The Tables include values of the coefficient of friction for polished surfaces of bismuth. They are taken from an earlier paper, but it must be observed that a much higher order of accuracy was arrived at in the measurements with glass and steel than in those made previously with bismuth. The sensitiveness of the apparatus has been improved and very much greater care taken to secure purity in the substances used.

Of the chemicals used, some have been made by one of us (I. D.) and all have been specially purified until chemical tests failed to detect any impurity. Impurities present in too small amount to be detected by chemical means will produce a measurable effect on the very sensitive surfaces employed. It will be noticed that the value for undecane falls slightly below the curve for paraffins. The specimen had a marked odour, and, according to our experience with, *e.g.*, octane, the smell of normal paraffins decreases as purification proceeds. We believe, therefore, that there was a residual impurity of vanishingly small amount in the sample of undecane.

We are specially indebted to Prof. R. Robinson, F.R.S., for some of the higher paraffins and their related acids and alcohols.

PART I.—EXPERIMENT.

The experimental method employed to measure friction was that described in the earlier papers. The sliding piece or slider had a spherical surface, which was applied to a plane surface, the plate, both surfaces being highly polished. From the middle of the slider a short stem projected, from which a fine thread passed over a light pulley to a light pan for holding weights. The thread was adjusted so that the pull on the slider was parallel to the plane surface.

The use of a curved surface has the advantage that some measure of definiteness is given to the area of true contact. Two plane surfaces, trued as carefully as possible, touch only at a few points, as Budgett's experiments prove.

Both slider and plate were enclosed in a small chamber through which a current of air was passed, which had been purified by exposure (in order) to sulphuric acid, solid potash, calcium chloride, and phosphorus pentoxide, and finally passed through a column of glass-wool. In the earlier experiments the air was purified simply by bubbling through sulphuric acid and then passing it through a column of glass-wool, to trap any possible spray, but the vapour of sulphuric acid was found very seriously to interfere with the results by acting itself as a lubricant, and it was necessary to introduce solid potash to remove it. When the surfaces were covered only by an invisible film of lubricant the vapour of sulphuric acid was found to lower the friction by no less than 17 per cent. Sulphuric acid is needed as a cleansing agent to remove organic impurities from the air.

Three solids were used, glass, steel and occasionally bismuth. The test of cleanliness, as was pointed out in an earlier paper, is the development of a high and constant value for friction. Each solid demands its own peculiar treatment to secure cleanliness; and when one embarks on a new solid, such as steel, it may be a month or more before a suitable method is found.

The "clean" state is one from which the grosser of the impurities which contaminate all naturally occurring surfaces have been removed. What remains, whether, for instance, there is left a film of condensed gas, is unknown. The state is, however, a perfectly definite one, in that it can be reproduced time after time with complete certainty. A plate of the glass used in these experiments is "clean" when its coefficient of friction is 0·94; the steel plates when clean gave the value 0·74. Other kinds of glass give values differing from 0·94. A negative may perhaps be ventured on. It is that "clean" surfaces are not the same as surfaces freshly produced by fracture. It is said that when steel is fractured under mercury the new surfaces amalgamate. "Clean" steel plates in clean air will not amalgamate.

Glass plates were cleaned by first washing with soap and water, rinsing under the tap, and allowing to dry by draining. They were then heated for about half an hour in a solution of chromic oxide in sulphuric acid, rinsed thoroughly under the tap (the plate being held with clean tongs) and allowed to drain. During draining, the lower edge of the plate rested upon two clean glass rods, the upper edge leaning against a clean glass bottle.

The glass sliders, being weighted with lead, could not be cleaned with chromic acid. They were, therefore, washed with soap and water, rubbed vigorously with the finger tips under a rapid flow of water until the "clinging" state was reached, and suspended in air until dry.

Steel plates and sliders were cleaned by washing with soap and water, rubbing vigorously with the finger tips in a stream of tap water until water wetted the entire surface, rinsing with perfectly dry pure alcohol, and allowing to drain in air. During the rinsing and draining processes the steel was not touched with the fingers at all, but held in tongs which had previously been cleaned by strong heating.

Variables.—The variables which have to be considered are the weight of the slider, the curvature of its surface, temperature, the thickness of the layer of lubricant, and the chemical nature of the lubricant and of the solids respectively. Of these one alone was not studied, namely, temperature, because the walls of the chambers which have been tried have given off vapours at moderate temperatures in quantity sufficient completely to vitiate the measurements. A chamber of special design is being constructed which will, it is hoped, relieve us of this difficulty.

The fundamental law of sliding friction is usually known as Coulomb's* law. As a matter of fact it was formulated 86 years earlier by Amontons;† we, therefore, propose to call it Amontons' law. According to it the friction is proportional to the weight of the slider and is independent of the area of contact. Coulomb regarded this law merely as an approximation and his view has been accepted by subsequent writers. We have made many measurements to verify the law, and they prove definitely that it is not an approximation, but an exact law, which holds so long as the surfaces, or rather the whole system, solid surfaces and lubricant, remain unchanged. Many solids suffer viscous flow from the pressure. This is the case when wood is used, and then the law ceases to hold. It is a rigid law for hard solids such as glass and hard steel.

According to Hertz's equation the area of contact varies as the cube root of the weight of the slider divided by its curvature. Careful measurements showed that the coefficient of friction (μ = friction divided by weight) is independent of the weight and of the curvature. It is, therefore, independent of the area. The values of μ are given in Tables I and II.

Table I.

Glass.					
Weight in grm.	21·63	31·64	41·63	51·63	61·63
Propyl alcohol...........	0·6321	0·6354	0·6301	0·6298	0·6352
Butyl „	0·6061	0·6042	0·6059	0·6076	0·6012
Amyl „	0·5821	0·5800	0·5833	0·5861	0·5847
Octyl „	0·5112	0·5126	0·5095	0·5093	0·5113
Heptylic „	0·4001	0·4018	0·4076	0·3982	0·3873
Caprylic „	0·3412	0·3392	0·3428	0·3413	0·3371
Heptane	0·6751	0·6703	0·6728	0·6741	0·6743
Octane	0·6551	0·6542	0·6508	0·6581	0·6548
Steel.					
Weight in grm.	15·46	25·46	35·47	45·47	55·49
Amyl alcohol	0·3658	0·3679	0·3708	0·3649	0·3651
Octyl „	0·2991	0·3032	0·2987	0·2999	0·3061

---

* Coulomb, 'Mem. de l'Acad. Roy. des Sci.,' vol. 10, p. 161 (1785).

† Amontons, *ibid.*, p. 206 (1699).

Table II.—Steel.

Radius of curvature (cm.)	14·70	3·58	1·78
Butyl alcohol	0·4018	0·4067	0·3917
Octyl „	0·3006	0·2991	0·2939
"Clean"	0·7408	0·7421	0·7427

Influence of the Quantity of Lubricant.

Fluid Lubricants.—Three methods of lubricating the surfaces were adopted:—

(1) A drop of lubricant was placed on the plate so that the slider stood in a pool of fluid. This is the *flooded* state.

(2) When a drop of a lubricant which has a sensible vapour-pressure is placed anywhere on a clean plate nothing detectable by the senses occurs. The drop to all appearances remains where it is placed without change. An invisible film, however, spreads from the neighbourhood of the drop so as to cover the whole plate. The presence of the film can be detected by the fall in friction. For reasons which will appear later (Appendix II) we call the invisible film the *primary film*, and the process by which it is formed *primary spreading.*

Obviously the invisible film would be subject to intense evaporation if the ordinary procedure were followed, in which a stream of clean air is passed through the chamber. This procedure was, therefore, modified as follows:—The lower part of the chamber was covered with a layer of fresh dry calcium chloride, and thoroughly washed out with a stream of dry air. The air stream was then cut off and it was found that clean plates remained completely uncontaminated in the chamber for 10 hours.

(3) When the lubricant has a sufficiently high vapour-pressure it can be deposited upon the surfaces by passing its vapour into the chamber. To accomplish this the stream of dry clean air was divided into two, one of which was bubbled through the lubricant whilst the other was led through a by-pass. The two streams were then led into a glass bulb provided with a device for thoroughly mixing them, and thence to the chamber. The proportion of the stream passing through the lubricant was varied by taps suitably placed and in this way the concentration of vapour in the chamber could be varied. In the case of one substance, ethyl alcohol, the concentration was determined directly by collecting samples of the stream as it entered the chamber and analysing them.

Primary spreading does not take place rapidly on a solid face. The friction falls slowly and finally reaches a steady value, it may be in an hour or so, which is uniform over the whole surface. It is this value which is recorded. The mechanism of spreading is discussed in Appendix II.

In Table III the values of the coefficient of friction (μ = friction divided by the weight) are given for flooding, for primary films, and for saturated vapour. The figures show that the friction is independent of the quantity of lubricant present, provided that there is enough to cover the surfaces with the invisible primary film.

Table III.

Lubricant.	Flooded.	Primary film.	Saturated vapour.
Glass.			
Ethyl alcohol	0·6512	0·648	0·6491
n-propyl alcohol	0·6301	0·6329	0·6283
n-butyl „	0·6061	0·6107	0·597
Amyl „	0·5853	0·5921	0·577
Caprylic „	0·5371	0·5356	—
Undecyl „	0·4450	0·4452	—
Butyric acid	0·5721	0·5793	0·5812
Valerianic acid	0·5259	0·5218	0·5309
Hexoic „	0·4653	0·4582	0·4648
Heptoic „	0·4051	0·4008	—
Caprylic „	0·3418	0·3412	—
Pentane	0·7102	—	0·7158
Hexane	0·6908	—	0·6913
Heptane	0·6753	—	0·6709
Octane	0·6557	—	0·6591
Steel.			
Butyl alcohol	0·3922	0·3906	0·3901
Amyl „	0·3751	0·3687	0·3716
Caprylic acid	0·2008	0·2073	—

It is obvious, since the primary film is in equilibrium with a drop of the parent fluid in a closed space, that its vapour pressure is the same as that of the free surface of the drop. Neglecting the very slight effect of the curvature of the drop in raising its vapour pressure we may, therefore, say that the vapour pressure of the primary film is that of a vapour saturated at the particular temperature. The critical value of friction, the value, that is to say, which is independent of the quantity of lubricant present is, therefore, that of faces so lubricated as to be in equilibrium with saturated vapour. The results obtained by using the lubricant as vapour confirm this view. The critical friction is also the lowest value which can be obtained in boundary friction.

The curves relating the coefficient of friction to the concentration of the vapour of ethyl alcohol are given in fig. 1, and the figures in Table IV. The concentration of the vapour is in gramme-molecules per litre.

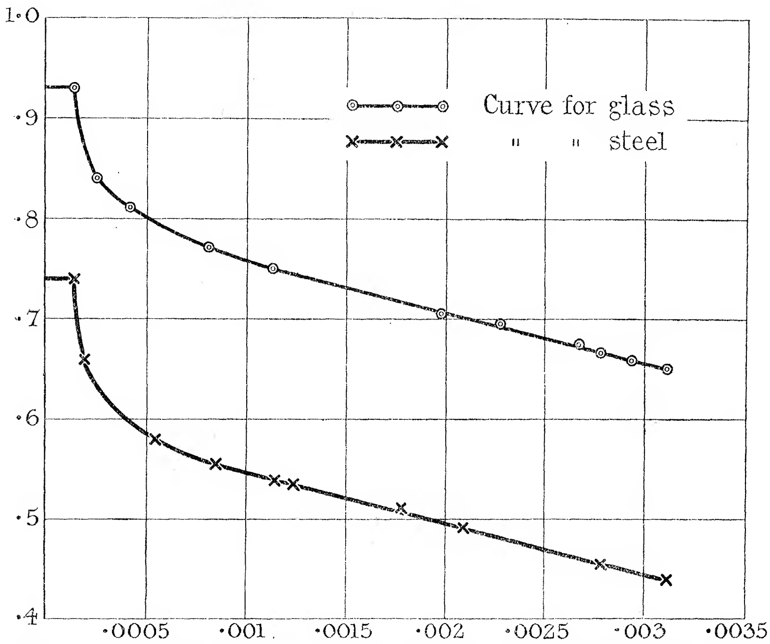

Fig. 1.—Abscissæ, number of gram-molecules of C_2H_5OH per litre of air. Ordinates, coefficient of static friction.

Table IV.—Ethyl Alcohol Vapour-Pressure Values.

Glass.		Steel.	
Grm.-mols. C_2H_2OH per litre.	μ.	Grm -mols. C_2H_2OH per litre.	μ.
0·00014	0·94 (clean)	0·00013	0·74 (clean)
0·00025	0·841	0·00018	0·661
0·00042	0·816	0·00053	0·580
0·00081	0·773	0·00085	0·555
0·001127	0·752	0·001146	0·543
0·001973	0·705	0·001225	0·538
0·00228	0·696	0·001783	0·512
0·002675	0·675	0·002102	0·489
0·00278	0·668	0·002781	0·454
0·002936	0·660	0·00311	0·441 (flooded value).
0·003111	0·651 (flooded value).		

The curves are straight lines save where the vapour-pressure is very low, when the results are liable to be upset by that degree of contamination from chance vapour which no amount of care in experimental procedure is likely to get rid of.

The fall in friction, therefore, is proportional to the concentration of chemical molecules of the lubricant in the gas phase, that is to say, each such molecule exerts the same influence as every other. The chances of any one molecule sticking to the solid surface will be proportional to the concentration in the gas phase, and therefore we may conclude that each chemical molecule in the film on the solid faces contributes an equal share to the fall in friction. This is not unlikely, since the fall in surface tension due to the presence of oleic acid on the surface of water is also proportional to the number of molecules of the acid per unit area.*

The most important features of these curves connecting vapour-pressure and the coefficient of friction are : (1) that they do not if prolonged meet the μ-axis at the clean value, though the measurement made with the lowest vapour pressure coincides with this value ; and (2) that the curves are parallel to each other over the linear portion.

The clean value obviously must form one end of the curves and in the figure they are continued so as to cut the μ-axis at this value. The first part of each curve is, therefore, horizontal. That is to say, a finite concentration of lubricant on the surface is needed to produce any fall in friction. It is well known, since Rayleigh pointed it out, that a finite concentration of a substance spread on the surface of water is needed to cause a fall in surface tension. Rayleigh suggested that this critical concentration occurs when the molecules spread on the surfaces are close enough to be within the range of each other's attractions and repulsions : when, that is to say, a continuous film is produced. Do the inflection points in the curves in fig. 1 also mark the formation of a continuous sheet ?

The parallelism of the curves for glass and steel shows that the effect which each molecule of the lubricant produces is independent of the nature of the solid surface to which it is applied. The fall in friction due to each molecule is, therefore, a pure function of its field of force, or, in other words, of its atomic configuration.

Solid Lubricants.

It is more difficult to follow the influence of the quantity of lubricant when it is a solid, because neither primary spreading nor the vapour phase can be made use of.

Surfaces were lubricated with solids either by smearing the lubricant over the plates with a glass rod or by depositing a thin film from solution in ether. A film of insensible thickness was obtained by polishing off as much as possible of the lubricant in the way described below.

In the case of paraffins and alcohols, as the ether evaporates the friction

---

* 'Roy. Soc. Proc.,' A, vol. 85, p. 317 (1913).

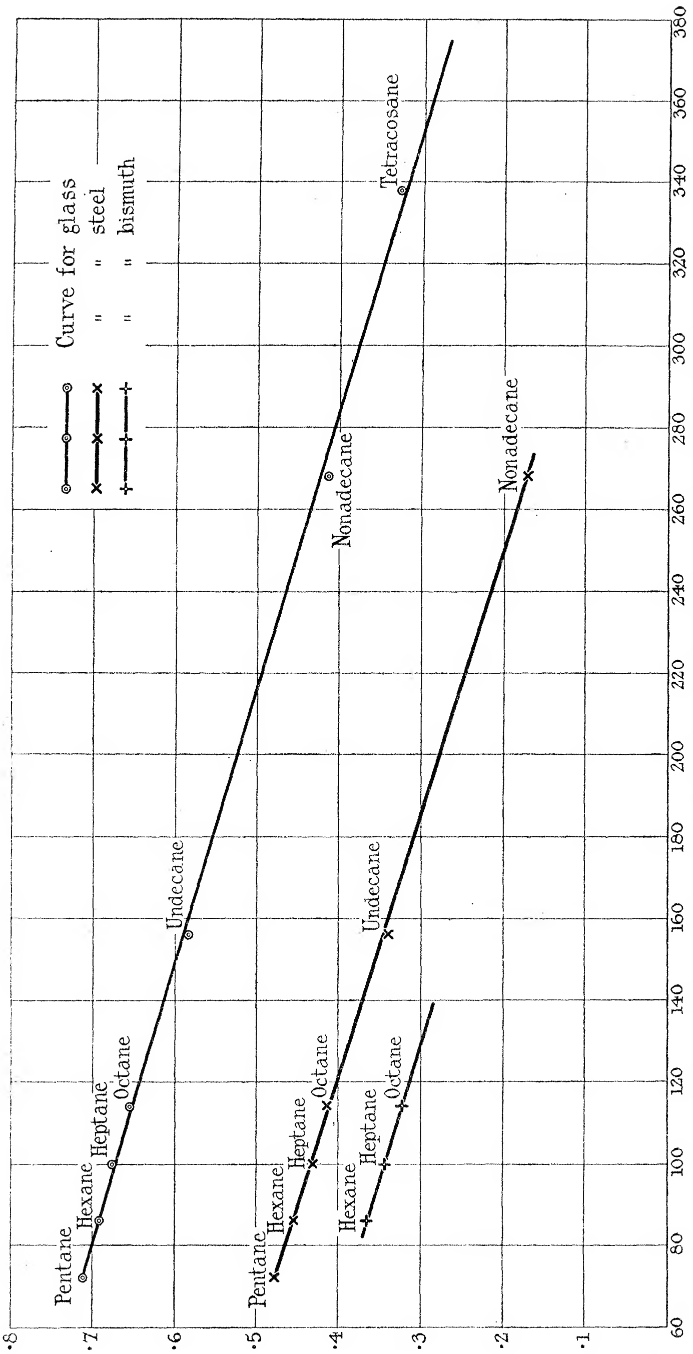

FIG. 2.—Abscissæ, molecular weight. Ordinates, coefficient of static friction.

falls until a very low value is reached, which coincides with the presence of the last trace of the solvent. The value persists only for a few seconds, the friction then rising to a steady value which is that of the pure substance. The final steady values lie on the curve for the series to which the lubricant belongs (figs. 2 and 3). The first set of values shows that for certain mixtures of solvent and solute, in this case ether and the particular paraffin or alcohol, the friction is much less than that obtained when ether is used by itself. The fact that a mixture of two substances may lubricate better than either when used alone was noted in an earlier paper.* The figures are given in Table V.

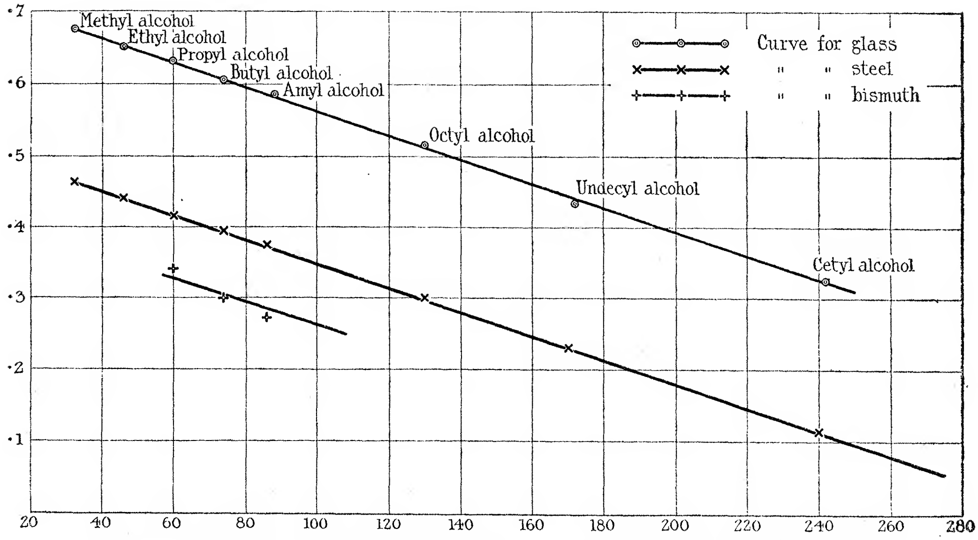

Fig. 3.—Abscissæ, molecular weight. Ordinates, coefficient of static friction.

The solid acids behaved differently. The first two used, namely, decoic acid and dodecoic acid, like the paraffins and alcohols, gave normal steady values for a film deposited from ether (fig. 4), and the polished film gave much lower values, but the higher acids from myristic acid onwards refused to give steady values at all. The explanation is simple. Examination of the surface under the microscope showed that the film of acid was highly crystalline and brittle, so that the slider broke away a crust. The observed friction, therefore, was due mainly to this crust and could be varied merely by moving the slider about on the surface before taking a reading. For example, values from $\mu = 0{\cdot}17$ to $\mu = 0{\cdot}52$ could be obtained with myristic acid. The crystallisation did not, however, seem to involve the primary film since very thin films deposited from ether were found to give values as low as polished films. Thus, with stearic acid the lowest value ($\mu = 0{\cdot}035$) obtained was got by depositing a film from an exceedingly dilute solution.

---

* 'Phil. Mag.' [6], vol. 40, p. 201 (1920).

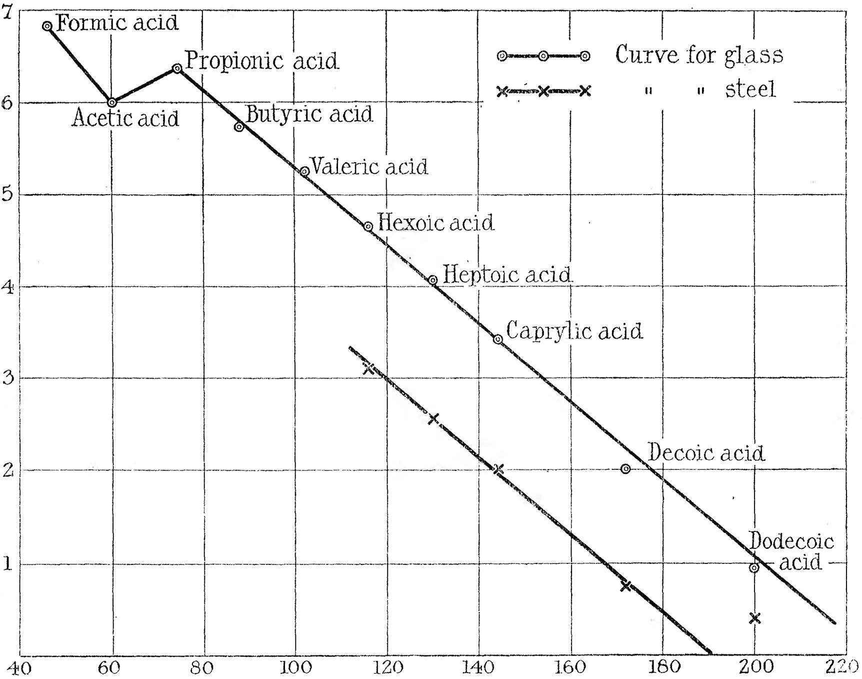

FIG. 4.—Abscissæ, molecular weight. Ordinates, coefficient of static friction.

Table V.—Solid Lubricants.

Lubricant.	Polished film.	Film deposited from ether.	
		Initial value.	Final value.
		Glass.	
Undecyl alcohol	0·017	0·0781	0·4472
Cetyl alcohol	0·019	0·0203	0·3284
Nonadecane	0·0467	0·0231	0·4119
Tetracosane	0·0321	0·0192	0·3251
Decoic acid	0·0632	0·0738	0·2006
Dodecoic acid	0·0404	0·0391	0·0983
Myristic "	0·0671	0·0382	Variable results, *e.g.*, myristic acid = 0·24 – 0·52 – 0·17 –0·31.
Palmitic "	0·0715	0·0340	Palmitic acid = 0·26–0·23 –0·37–0·8–etc.
Stearic "	0·0318	0·0296	
		Steel	
Nonadecane	—	0·0213	0·1783
Cetyl alcohol	—	0·0182	0·1126
Palmitic acid	—	0·0113	Value irregular.

The increase in the hardness of the crystals with increase in molecular weight probably accounts for the difference in the behaviour of myristic, palmitic and stearic acids, from that of decoic and dodecoic acids.

Attempts were made to polish off both fluid and solid lubricants, with interesting results. For this purpose fragments of fine linen were used which had been exhausted of all "greasy" matter by prolonged extraction with benzene. The linen was regarded as being clean when the friction of a clean surface was not lowered after having been vigorously rubbed with it. In all the operations the linen was not held in the hands but by clean tongs. When the lubricant was a fluid, polishing completely removed it from the surfaces, the friction rising to the clean value, but it was not found possible to polish off a solid lubricant. Polishing a plate covered with a solid lubricant until nothing was visible under a microscope left a surface which gave a very low value for friction. If the normal value of the particular lubricant be that which lies on the curve for its particular chemical series, then polishing produced an abnormally low value. An interesting case is that of undecyl alcohol. This substance melts at 11° C., it was easy, therefore, to apply it either in the fluid or solid states. In the former the alcohol could be completely polished off a surface, whilst in the latter polishing merely served to produce an invisible film having an abnormally low friction. Abnormally low values are also obtained when fluid lubricants are polished, but they are transitory. The figures for polished films appear in Table V.

Influence of Chemical Constitution.

Table VI gives the coefficient of friction of each substance for glass on glass and steel on steel. The values for bismuth are taken from an earlier paper.

In figs. 2, 3, 4 and 5 these values are plotted against molecular weight. It will be seen that for each chemical series, and for each solid, the curve is a straight line. The equation is, therefore,

$$\mu = b - aM,$$

where M is molecular weight and a and b are parameters. The effect of the nature of the solid face is unexpectedly simple. In changing from glass to steel the curve for a series is merely moved parallel to itself, and in moving from steel to bismuth there is a further shifting. Therefore, in the equation the parameter a is independent of the nature of the solid face and dependent only on chemical type, varying from one chemical series to another. The parameter b, on the other hand, is dependent upon the nature of the solid face as well as upon the chemical series.

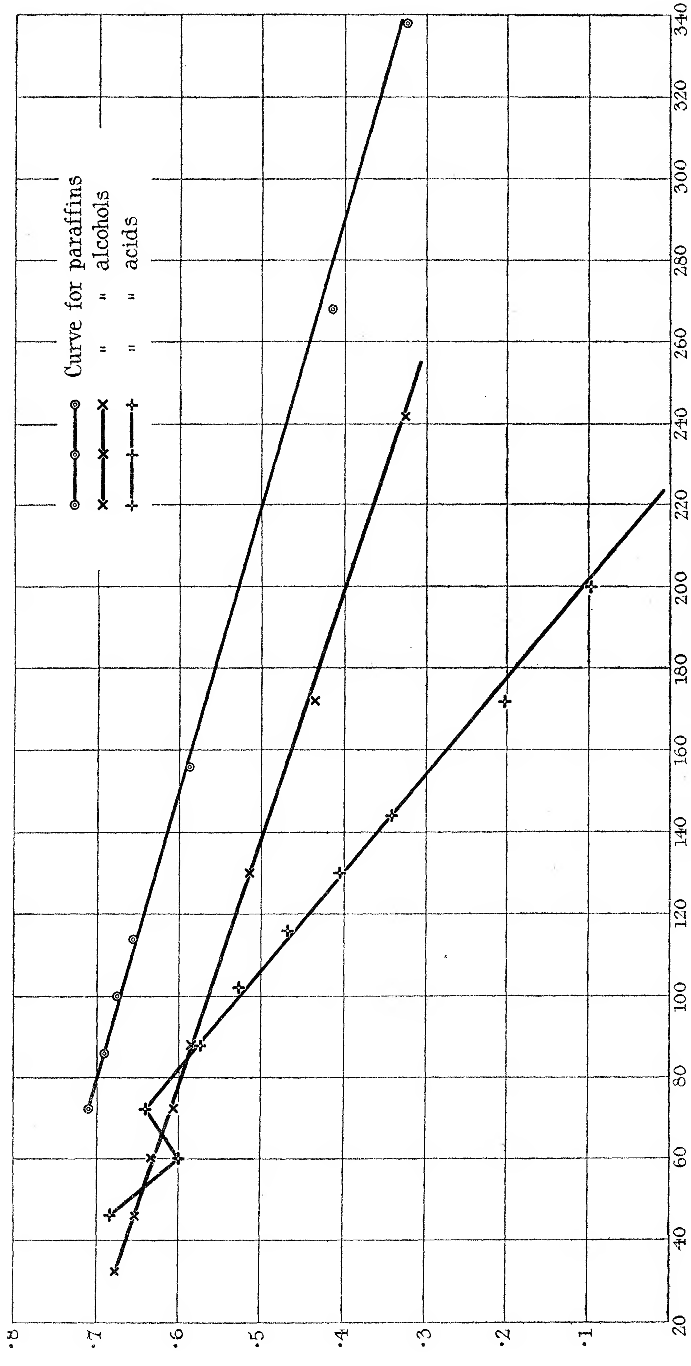

Fig. 5.—The three curves for glass.

Table VI.

Lubricant.	Glass.	Steel.	Bismuth.
n-pentane	0·7102	0·4763	—
n-hexane	0·6908	0·4528	0·37
n-heptane	0·6751	0·4307	0·346
Iso-heptane	0·6683	—	—
n-octane	0·6552	0·4112	0·32
Undecane	0·5903	0·3421	—
Nonadecane (deposited from ether)	0·4119	0·1785	—
Tetracosane (deposited from ether)	0·3251	—	—
Methyl alcohol	0·6772	0·4610	0·29
Ethyl „	0·6512	0·4408	0·32
Propyl „	0·6301	0·4173	0·34
Butyl „	0·6061	0·3924	0·30
Iso-butyl „	0·6273	—	—
Amyl „	0·5854	0·3752	0·27
Octyl „	0·5176	0·2981	0·25
Caprylic „	0·5373	—	—
Undecylic „	0·4455	0·2298	—
Cetyl „	0·3253	0·1143	0·17
Formic acid	0·6823	—	0·45
Acetic „	0·6003	—	0·40
Propionic acid	0·6387	—	3·31
Butyric „	0·5721	—	—
Valeranic „	0·5259	—	0·28
Hexoic „	0·4654	0·3108	—
Heptoic „	0·4051	0·2556	—
Caprylic „	0·3417	0·2003	0·19
Decoic „	0·2006	0·0741	—
Dodecoic „	0·0983	—	—
Myristic „	Readings for smeared faces variable.		
Palmitic „			
Stearic „			

When other variables are not involved the value of the coefficient of friction is always in the order glass > steel > bismuth. For the two metals this is in the order of their respective hardness. But it does not depend only on hardness, since the steel used was harder than the glass.

The influence of the chemical nature of the solid face is unexpectedly simple in other ways. Thus, for the three lubricants tried, when the slider is of glass and the plate of steel, the value of μ is exactly midway between that for glass on glass and steel on steel. The following figures illustrate this:—

Table VII.

Slider.	Plate.	Lubricant.		
		Butyl alcohol.	Amyl alcohol.	Octyl alcohol.
Glass	Glass	0·606 } mean 0·4992	0·585 } mean 0·48	0·5176 } mean 0·4078
Steel	Steel	0·3924	0·375	0·2981
Glass	Steel	0·493	0·48	0·41
Glass	Glass	0·606 } mean 0·453	—	0·5176 } mean 0·3838
Bismuth	Bismuth	0·30	—	0·25
Bismuth	Glass	0·451	—	0·38
Steel	Steel	0·3924 } mean 0·3464	—	0·2981 } mean 0·274
Bismuth	Bismuth	0·30	—	0·25
Bismuth	Steel	0·348	—	0·27

To get this simple result the curved surface must be of the softer material. If it be of the harder the figures are different because the softer surface is cut.

PART II.—THEORY.

The current view that friction is due to the interlocking of asperities dates back to Coulomb. The asperities of a polished face are no doubt insensible, but earlier writers conceived of them as real elevations of the surface. Herschel, for example, writes: "A surface artificially polished must bear somewhat the same kind of relation to the surface of a liquid, or a crystal, that a ploughed field does to the most delicately polished mirror.*

Rayleigh† came to the conclusion that the difference between a fluid and a polished surface was not great, the elevations of the latter being of molecular dimensions. Beilby's work on polishing is well known. It confirmed Rayleigh's view.

Coulomb's hypothesis, that friction is due to asperities acting like inclined planes, implies at the limit that the actual surface of the solid is frictionless. This does not seem to be possible, since we know that the surface of a solid is the locus of a powerful field of attraction which is the cause of capillary phenomena, and this attraction, though it may be modified by the film of contamination on all naturally occurring solid faces, is not destroyed by it, otherwise, for example, a drop of water would not cling to a glass rod.

The view taken in earlier papers‡ is that friction is due to molecular attraction operating across an interface, in short, to cohesion. If matter were continuous, and if the equipotential surfaces of its superficial attraction field were parallel to a plane surface, it would be frictionless. But matter is discontinuous, and it is to this that friction is due. The asperities required by Coulomb are in fact the atoms and molecules, for, owing to the short range of molecular and atomic attractions, the equipotential surfaces are by no means simply parallel to the general material surface. The action of a tangential force does not merely move the atoms and molecules in their own tangent planes, but also rotates them and produces movements of compression along the normal, and the friction—the tangential reaction as French writers call it—is the sum of the resistances to displacements of the centres of mass and to rotation.

---

* 'Enc. Met., Art. Light.,' 1830, p. 447.

† 'Polish,' Royal Institution, March, 1901.

‡ 'Phil. Mag.' [6], vol. 38, p. 32 (1919); *ibid.*, 49; [6], vol. 40, p. 201 (1920).

When two solid faces are separated by a layer of lubricant the molecules of the latter must be supposed to be highly oriented. The fact that there is a finite resistance to slip shows that the substance of the layer, though it may be formed from material which is fluid at the temperature of observation, has lost its fluidity. This can be due only to the influence of the attraction fields of the solids, which destroys the random arrangement of the molecules which permits of fluidity, and substitutes for it a configuration in which the potential of a molecule is a function of its position and orientation.

The system, therefore, is one which varies rapidly in state along a normal to the solid faces, supposed to be plane, but is homogeneous along surfaces which are parallel to the solid faces. It may be regarded as consisting of a series of imaginary surfaces each having different mechanical properties. When the two solid faces are identical in nature and parallel to each other there may be supposed to be symmetry about a plane surface midway between them, such that surfaces equidistant from this median plane will have identical properties.

When a tangential force is applied there will be "give" at each plane, which will increase with the growth of the applied force until a yield point is reached, when slipping occurs, and, owing to the heterogeneity of state along the normal, the slip is confined to one, or at most two, planes.

The fact that the friction of surfaces flooded with lubricant is the same as that of the same surfaces when covered only with a primary film shows that the layer of lubricant actually present between the opposed faces is identical in thickness and structure in both cases. When the lubricant is in excess this layer will be that which can support the weight of the slider owing to the operation of capillary forces. Let a surface be drawn in the interior of a mass of lubricant resting on a plane solid face at a distance from the solid face equal to the thickness of a primary film. Such a surface must have peculiar significance in lubrication. It is easy to see why this is so. When a fluid such as, *e.g.*, benzene is poured over a clean surface of water in a vessel, covered so that the space above may become saturated with benzene vapour, it will be noted that, if the sheet of benzene is not too thick, say about 1 mm., it ruptures in places, and contracts to form lenses which are in equilibrium with a composite surface covered with an invisible film of benzene. The continuous sheet of benzene is, therefore, unstable, and it ruptures in the plane which separates the primary film from the mass of the fluid; the benzene below this plane remains adherent to the water, while the benzene above contracts on itself to form lenses or a single lens. The surface mentioned above is, therefore, at that critical distance from the water face at which the attraction of benzene for itself is greater than its attraction for water. It marks what might be called a natural flaw in the structure of the benzene. For this reason it may be expected to be a natural plane of slip when tangential stress is employed, and therefore to be of fundamental importance in lubrication.

Consider two solid faces each covered with a primary film, and let them be applied the one to the other, and let the area of one face be much greater than that of the other. The layer of lubricant may either consist of the two primary films or be greater or less than this, the thickness being determined by the pressure and capillary forces. If it be greater, then the excess must be drawn in between the solid faces by capillary forces from the primary film elsewhere on the surfaces. The balance of probability is that the layer is not thicker than two primary films, for capillary attraction might be expected to draw in more from a flooded face than from a face covered only by a primary film, and the equality in the coefficient of friction proves that this does not happen. Measurements made with sliders loaded excentrically point strongly to the same conclusion (Appendix I). It is not likely to be less than two primary films in thickness, because the coefficient of friction in that case would not equal the flooded value, as the study of the relation to vapour-pressures shows.

The parameter a measures the contribution of the solid faces to the friction. When two different solids, 1 and 2, are employed the contribution of each, as experiment shows, is $\frac{1}{2}a_1$ and $\frac{1}{2}a_2$, respectively. Therefore each solid face contributes its effect upon the friction independently of the other. The question, however, to which an answer is not readily forthcoming is, Why does the nature of the solid influence the friction of lubricated surfaces at all?

The slipping which occurs when the stress reaches a certain intensity may be due either to a general breakdown of structure in the lubricant or the structure may persist and the slip be confined to a plane, which is probably the plane midway between the solid faces *when these are composed of the same material.* The fact that there is no break in the curve connecting friction with molecular weight when the lubricant becomes a solid is against there being a general breakdown of structure, for it is unlikely that tangential stress would confer upon a film of a solid lubricant the property of fluidity. A further objection is found in the fact, noted by many writers, that kinetic friction is equal to static friction and is independent of the velocity. This can only mean that static friction measures the maximum tangential stress which a certain molecular structure is capable of bearing. If the structure broke down during relative motion the stress must, we conceive, be changed in amount.

Let us assume, then, that slip is confined to one plane and that the friction measures the tangential reaction at this plane. The reaction depends, as we have seen, not only upon the chemical nature of the lubricant, but also on that of the solids. The field of attraction of the latter must therefore make itself felt in a decisive way at the plane of slip. In the language of the classical theory of capillarity, the range of the force of attraction must be at least equal to half the thickness of the layer of lubricant.

The point at issue will be made clearer by considering this fact in terms of a particular theory of the structure of primary films. When a substance such as, *e.g.*, oleic acid is allowed to spread over water no fall of surface tension is produced until the concentration of the acid on the surface has reached a certain very small value. Rayleigh suggested that this concentration marks the point when the acid forms a continuous layer one molecule thick, when, that is to say, the molecules of the acid are close enough together to be within the range of each other's attraction and repulsion. Increase in concentration of the acid causes the surface tension to fall until a second point is reached, at which further additions cease practically to produce any further effect. The surface is now saturated with the acid and any excess merely collects into lenses of acid in mass. The second point of inflection, therefore, is the point at which the primary film is completely formed. Rayleigh* suggested that at the second point the layer of acid is two molecules thick.

Rayleigh's first suggestion has been accepted by all who have since worked at the subject. His second suggestion, namely, that the primary film consists of two layers of molecules has not found favour. The view which has replaced it we owe to Devaux,† who considers that the primary film is always of a single layer of molecules, and that the second point mentioned above occurs when the molecules are packed as closely as possible. The film, in short, is regarded as an elastic structure, which is at its maximal extension when it first begins to affect the surface tension, and at its maximal tangential compression when the surface is saturated. Further compression then results in some of the molecules mounting on top of the layer. This is the monomolecular theory of the structure of these surface films. One of us pointed out that in such films and at all interfaces between immiscible fluids the molecules must be highly oriented with respect to the surface by the asymmetrical field of attraction.

---

* 'Phil. Mag.' [5], vol. 48, p. 334 (1899).

† 'Rev. Gén. des Sciences,' 4, February, 1913.

The theory of surface films has been developed on these lines in a striking way by Langmuir* and Hawkins.† Consider, for example, an acid like palmitic acid. Each molecule consists of a chain of carbon atoms with attached atoms of hydrogen, with a carboxyl group at one end. The carboxyl group is soluble in water, for whereas the paraffins are typically insoluble, the related acids of the lower members of the series are soluble. The carboxyl group may, therefore, be regarded as being much more strongly attracted by water than is the chain of carbon atoms. Langmuir, therefore, pictures a primary film of palmitic acid on water as being composed of molecules attracted to the water by the carboxyl group only, the carbon chain being disposed at right angles to the water surface. The forces of attraction he considers to be of such short range as to extend only from one atom to its immediate neighbours. The influence of the attraction field of the water would, therefore, not extend beyond the atoms of the carboxyl group, the rest of the molecules, consisting of the carbon chain, would be wholly beyond its range. This represents the monomolecular theory pushed to its limits. Imagine the attraction of a solid limited in the same way to the carboxyl group, friction would depend only upon the lubricant and would be independent of the nature of the solid, for cohesion at the plane of slip would then be due only to the terminal group of the chain, namely, the CH_3 group. We know, on the contrary, that the friction is dependent upon the nature of the solids, and that, therefore, the field of attraction of the solids does not merely serve to anchor the molecules of the lubricant, but must also, in some way, make itself felt at the plane of slip.

One of us has urged that the range of attraction in gases or vapours is quite different from what it is in condensed states of matter. In gases or vapours the range is no doubt very short, so short as to be comparable to the distance between the atoms of a molecule. In fluids, however, there must be an irradiation of effect. If the field of one atom or molecule tends to orientate the axes of neighbouring atoms or molecules, these in turn will tend to orientate other molecules, and so the effect will spread until, in the case of a fluid, it is finally lost in the heat motions. Such an irradiation of effect must be specially great at interfaces where the general attraction field is itself oriented, and it is this extended range, and not the absolute range of attraction in a vacuum, which is operative in the theory of capillarity. The solids may be supposed to modify cohesion right through a layer of lubricant by spreading of strain in this way, even though the *absolute* range of their attraction may be as small as Langmuir supposes it to be.

---

* 'J. Am. Chem. Soc.,' vol. 39, p. 1848 (1917).

† *Ibid.*

The most puzzling questions are, Why should friction fall with increase in the molecular weight of the lubricant, and why should it vary directly with the normal pressure? Coulomb took the fact that friction is independent of the area of the surfaces to prove that it could not be due to cohesion because this obviously varies with the area. Cohesion, he admitted, must play some part, but a small part compared to that due to the "engaging" of asperities. Amontons' law, in that case, would be only an approximation, as Coulomb indeed took it to be. It is, on the contrary, a rigid law, save in those cases in which the traction alters the texture of the solids.

There seems to us to be an unanswerable objection to Coulomb's theory. Let us suppose that the molecules of the lubricant are anchored by the attraction fields of the solid, and that they reduce friction by reducing the inequalities of the solid surfaces. The capacity for reducing inequalities, or filling up depressions, might well be supposed to increase as the molecules got larger, but there are no serious differences in the size of molecules of paraffins and the related acids or alcohols which have the same number of carbon atoms. In other words, the theory fails wholly to explain the connection between chemical constitution and lubrication.

A picture which, however, is purely qualitative, of how molecular weight may influence lubrication is afforded by the assumption that the molecules of the lubricant are oriented by the attraction fields of the solids so that their long axes are at right angles to the solid faces. To give precision to the picture let us assume that the layer of lubricant is composed of two primary films the plane of slip being between them. Each CH_2 group which is added to the molecule lengthens the carbon chain and, therefore, increases the distance of the plane of slip from the solid faces. But the external tangential force is applied at the solid faces and as the distance is increased the moment of the force at the plane of slip will be increased. Lengthening the carbon chain will, therefore, have an effect similar to the lengthening of a rod when a couple is applied at the ends.

We are, however, no nearer explaining why each carbon atom added to the chain should produce the same effect. If the chain were straight the moment of the tangential force would be proportional to the number of carbon atoms, but it is certain that the chain is either a zigzag or a flat spiral. We are almost driven to the conclusion that in the primary films the atomic pattern of the molecules suffers rearrangement, somewhat like that which occurs in crystal formation. The primary film in a sense may be said to be crystallised, but the pattern is determined by the attraction fields of the solids. The view that a sub-crystalline structure obtains even at interfaces between immiscible fluids was put forward by one of us many years ago. It helps us to understand how the presence of hydroxyl and carboxyl groups may influence lubrication by modifying the attraction field of the solid.

It must be admitted that no explanation of Amontons' law is forthcoming. Like Hooke's law, and the simple linear relation between the concentration of oleic acid on the surface of water and the fall in surface tension, it is probably one of those laws of average values which mask the innate complexity of matter. The most promising way of stating the law is as follows :—For the same solids and the same lubricant the tangential reaction (the friction) per unit area is dependent only upon the pressure. The area now disappears from the equation since it occurs both as numerator and denominator.

An explanation of this relation will be forthcoming only when the theory of boundary friction is developed by some one fully cognisant of the theory of elastic solids. We content ourselves with a suggestion. An equipotential surface drawn above the general plane surface of a solid is not likely to be a plane, because the solid is particulate and each particle is surrounded by a complex field of force. Any equipotential surface is a frictionless surface in the sense that a particle of matter small enough not to distort the surface could be moved over it without effort. In measurements of static friction we can neglect inertia, therefore, if there were no normal pressure due to an external force on the particle, any force having a tangential component would cause it to move over the equipotential surface on which the particle is maintained by attractive and repulsive forces. If there were a normal pressure due to an external force a tangential force would experience resistance to the motion of the particle and the resistance would be proportional to the pressure.

The work done by the external force in the condition of static friction is absorbed by the elastic forces between the atoms and molecules of both lubricant and solid. If the force be applied with sufficient slowness the action is probably thermodynamically reversible, the local cooling or heating effects being reversible. The strain produced by the external force will consist in displacements of the centres of mass and in rotation of atoms and molecules When slipping occurs, that is to say in the condition of kinetic friction, we picture the slip as being confined to one plane because the yield point of this plane has been reached. The yield point fixes a limit and therefore (as many observers, from Coulomb onwards, have noted) the tangential reaction of kinetic friction is equal to that of static friction. It follows that the strain during the application of the external force is the same in both states, and the dissipation of energy in kinetic friction is due to the recovery from the strained position of the atoms and molecules which occurs immediately *behind* the slider.

The curves connecting friction and molecular weight, if prolonged, will meet the base line; therefore, when the molecular weight is increased sufficiently static friction vanishes. This point is difficult to observe, for the following reasons. When lubrication is bad the motion which occurs when the slider breaks away is rapid, as though the tangential force necessary to cause the breaking away were in excess of that needed to maintain movement.* As lubrication is improved the motion takes on more and more the nature of a slow glide, which may be so slight as to be barely detectable. Ricinoleic acid, which is a fluid at ordinary temperatures and a very good lubricant (*cf.* 'Phil. Mag.' 40, 201, 1920), does abolish static friction in the sense that the smallest tangential force which could be applied with our apparatus, namely, that due to the light aluminium pan (= 0·6 grm.), caused the heaviest slider to glide very slowly.

Solid lubricants which should lie on the curve below the base line seem to give finite, but very small, values for static friction. There may, therefore, be a discontinuity between the fluid and solid states in this region. The apparatus, however, was not sufficiently sensitive to settle the point. The values obtained are given below, for what they may be worth:—

Tetracosane on steel	$\mu =$ 0·085
Dodecoic acid on steel	0·031
Dodecoic acid on steel (polished film)...	0·026
Palmitic acid on steel	0·029
Stearic acid on steel	0·023

---

* This at first sight appears to contradict the equality between kinetic and static friction so often observed, but this equality has been noted in experiments in which both surfaces have had considerable extension. When the surface of the slider is curved and that of the plate plane, motion of the slider tends to cause it to mount on a thickened pad of lubricant.

Appendix I.

Treatises on mechanics deal exclusively with frictionless systems. Painlevé, in 1895, took up the question whether it is possible to develop a general theory for systems with friction analogous, for example, to the application of the equation of Lagrange. His analysis led him to the conclusion that Amontons' law contradicts the equation of motion of a solid, at least in certain realisable cases. This conclusion led to a controversy maintained by French and German writers for about 15 years, which turned on the question whether the condition of absolute rigidity postulated by Painlevé was not responsible for his paradoxical conclusion.

Amongst the many papers is one by Chaumat,* in which he states that the friction depends not only on the pressure, as Amontons' law states, but also on the degree of asymmetry of the loading. An oval slider, for example, which has a weight placed near one extremity will not conform to the law. In our own experiments the loading was always symmetrical in the case of the steel sliders, which were themselves accurately turned, and any extra weight was added in the shape of circular discs. Loading was not, however, always exactly symmetrical in the case of the glass sliders, since the melted lead with which they were weighted tended to run into an irregular pattern. Measurements were, therefore, made with sliders loaded as unsymmetrically as possible, the weight of lead being either wholly in front or wholly behind the point of application of the external force. In the first case the slider was tilted forward, and in the second case backward by the weights.

The following Table gives flooded values of μ for forward-loading, backward-loading and symmetrical loading, in which the external force was applied so as not to cause the slider to rock sensibly :—

Loading.	Lubricant.	
	Octyl alcohol.	Caprylic acid.
Forward	0·5192	0·3423
Backward	0·5028	0·3356
Symmetrical	0·5176	0·3412

The value for the backward loading is slightly but definitely lower. This, however, does not in our opinion confirm Chaumat's conclusion. Consider a curved slider standing in a pool of lubricant. Chance oscillations tend to bring excess of lubricant between slider and plate in the region of "contact."

---

* 'Comptes Rendus,' vol. 136, p. 1634 (1903).

General earth vibrations, due for example to the slamming of a door in the building, were found sometimes completely to upset the readings. A backward-loaded slider was found to be mechanically unstable to vibration. Readings were obtained only by exercising the utmost patience. A backward tilted slider is like a backward tilted plane surface, in that any movement forward due to small vibrations will tend to thicken the layer of lubricant. We conclude, therefore, that the slightly lower value of friction given by backward loading was due to secondary causes.

This is confirmed by the fact that when lubrication was by a primary film, there being no excess of lubricant on the surfaces, the friction was independent of the nature of the loading, as the following values for heptylic alcohol show:—

Forward	0·4090
Backward	0·4088
Symmetrical	0·4050

This result would seem to prove that in lubrication by primary film the slider is not seated on a thickened pad of lubricant drawn in by capillary forces. The layer is indeed composed of a double primary film.

APPENDIX II.

When a drop of a single pure chemical substance is placed upon a clean surface of water one or both of two things may follow, namely, the spreading from the drop of an invisible film, and the spreading of the drop itself by actual flattening to form a layer which, at any rate at first, is of sensible thickness. These processes are distinct, because the first may occur without the second. Spreading of the drop itself occurs only when the surface tension of water is greater than the sum of the tensions of the upper and lower surfaces of the drop. It is this kind of spreading which is contemplated in the classical theory of capillarity. Normal paraffins with more than eight carbon atoms, and stable saturated substances like carbon tetrachloride, do not manifest this kind of spreading; but, if they have a sensible vapour pressure, an invisible film is formed, not directly from the drop, but through the mediation of the vapour phase. The formation of the insensible film is called primary spreading, whilst the flattening out of the drop is called secondary spreading.*

There can be no manner of doubt but that primary spreading on solid faces occurs through the intervention of the vapour. Only those lower members of a series which have a sensible vapour pressure manifest it, and, as the molecular weight increases, and the vapour pressure decreases, the film forms more and more slowly. The time taken, after the drop was in position, for the friction to become uniform all over the plate at the critical or "flooded" value was, in minutes:—

---

* 'Roy. Soc. Proc.,' A, vol. 88, p. 313 (1913); 'Phil. Mag.,' vol. 38, p. 49 (1914).

Lubricant.	Glass.	Steel.
Methyl alcohol..................	5	—
Ethyl ,, ...	5	—
Propyl ,, ...	10	—
Butyl ,, ...	20	20
Octyl ,, ...	35	40
Acetic acid	5	—
Butyric acid	10	—
Heptylic ,, ...	40	—
Caprylic ,, ...	50	45
Undecane	5	5

The gradual formation of the film is shown by the following diagram, in which the position of the drop of butyl alcohol on the steel plate is indicated by a circle, and the figures give the value of the coefficient of friction at the place where they are printed, ten minutes after the drop was placed on the plate.